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# Long chain branching on linear polypropylene by solid state reactions

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## Abstract

A method was developed for the long chain branching (LCB) of isotactic polypropylene (iPP) via modification in the solid state. PP long chains have been linked as branches to the original linear iPP chains using solid state reactions in the presence of a free radical initiator and a multifunctional monomer (co-agent). The modified samples of branched iPP were characterised by gel permeation chromatography (GPC) and rheological measurements. Several methods were applied in order to estimate indirectly the extent of branching. A ranking was made of the co-agents according to their ability in inducing LCB as opposed to cross-linking and degradation of iPP. The furfuryl sulphide (FS) showed the highest efficiency for the branching reaction, while the divinylbenzene (DVB) is not suitable for branching.

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**Keywords:** Isotactic polypropylene; Long chain branching; Peroxide modification; Co-agents; Melt strength; Thermoforming

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## 1. Introduction

iPP is the commodity polymer with the largest share in the present market. iPP has many advantageous properties when compared to other commodity thermoplastics, such as polyethylene, in all its forms, and PVC: it has high melting point and low density, it shows excellent chemical resistance, high tensile modulus, it costs less to produce and does not present the difficulties in recycling that are associated with PVC. Commercial iPP is produced via

Ziegler–Natta or metallocene catalysis, consists of highly linear chains and has a relatively narrow molecular weight distribution. As a consequence, the iPP has relatively low melt strength and rather poor processing characteristics in processes where the type of flow is predominantly elongational. Such processes are, e.g., foaming, thermoforming, extrusion coating, and blow moulding. In order for iPP to be used in these forming processes, modification of the polymer is necessary to enhance its strain hardening behaviour in elongation. Broad or bimodal molecular weight distributions can result in strain hardening. However, the most efficient way to enhance the melt strength of polymers with linear chains is by grafting long chain branches (LCB) on

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them. It is expected that the position of iPP in the plastics market will become even more prominent if the elongational flow behaviour of its melt is improved [1].

Much effort in producing branched PP has been made in the polymer industry and several commercial grades of high melt strength PP are available. These are mostly produced by grafting long chain branches on the PP linear backbone, either by electron beam (EB) irradiation [2] or in the melt by using peroxides with relative low decomposition temperature [1]. These methods produce LCB-PP with broadened molecular weight distribution and complex branch structures. There are also some reports on the direct synthesis of long chain branched PP: using metallocene catalysis either directly [3] or via the addition of pre-made PP macromonomers [4]; using conjugated diene monomers [5]; via the metallocene-mediated polymerisation of PP in the presence of T-reagent *p*-(3-butenyl)styrene [6,7]. The latter article includes a good review of these methods to synthesise LCB-PP. Another conceivable method is the modification by peroxide reactions in the solid state in the presence or not of a co-agent [8].

The aim of the present paper is to investigate whether it is possible to produce long chain branched isotactic polypropylene via solid state modification using a peroxide in the presence of a co-agent. For this work we have chosen a series of co-agents with different free radical reactivity and solubility in iPP. A further goal is to find which types of co-agents from this series are most effective for branching of iPP and to establish some simple criteria for the choice of the co-agent to be used.

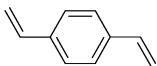
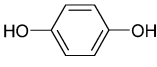
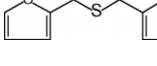
## 2. Grafting of long chain branches on linear PP

Three co-agents were used in this research in combination with the organic peroxide *tert*-butyl peroxybenzoate (TBPB) to produce LCB on iPP. The co-agents were bifunctional monomers, which are able, using their multiple functional groups, to react with macro-radicals formed on the neighbouring iPP chains and form chemical bridges between them. Their chemical structure together with their solubility parameter,  $\delta_s$ , calculated by the group contribution method [9], are reported in Table 1.

Scheme 1 depicts a generally accepted mechanism for the reactions, based on the available information in the literature [10–15]. Primary radicals formed by

Table 1

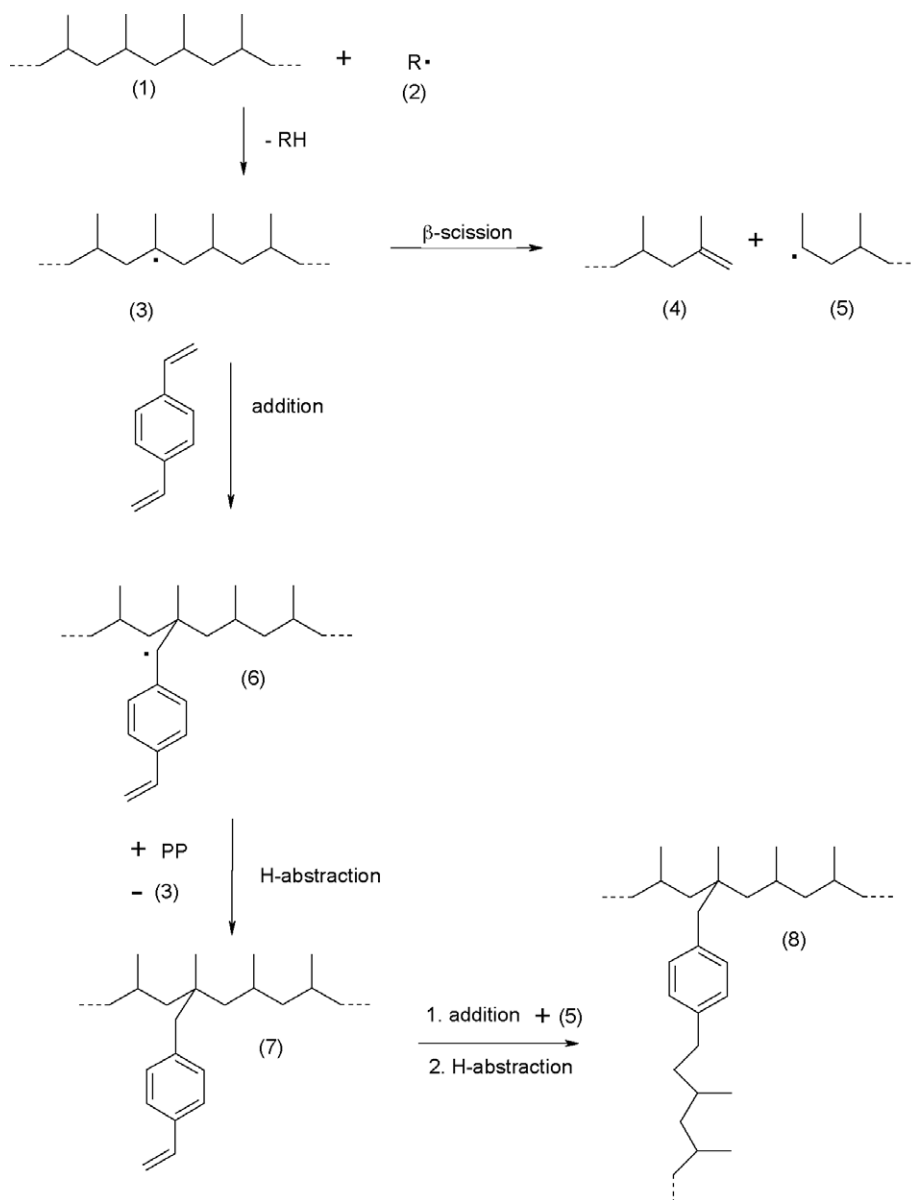
Chemical structure and solubility parameter,  $\delta_s$ , of the co-agents

Chemical name	Abbreviation	Chemical structure	$\delta_s$ (cal/cm <sup>3</sup> ) <sup>0.5</sup>
<i>tert</i> -Butyl peroxybenzoate	TBPB	<chem>C6H5COOOC(CH3)3</chem>	–
Divinylbenzene	DVB		8.8
1,4-Benzenediol	RES		15.1
Furfuryl sulphide	FS		10.7
Polypropylene	iPP		7.4

The values of  $\delta_s$  of the co-agents must be compared with that of iPP to rate their compatibility.

the decomposition of the peroxide (2) react with iPP (1) to yield macro-radicals (3). Radicals of different reactivity (primary, secondary and tertiary) are generated, but for the sake of simplicity only tertiary ones are depicted in Scheme 1. These macro-radicals can, in principle, undergo  $\beta$ -scission of the chain towards the formation of an unsaturated iPP chain end (4) and a secondary radical (5). At the same time, the macro-radicals (3) can react by addition with the unsaturated monomer (DVB is used as example in the scheme) to yield the corresponding adduct (6), which can further react with the secondary macro-radical in its vicinity to form the desired LCB-PP. Another route is that the adduct (6) forms the corresponding grafted product (7), i.e., PP-g-DVB, after abstraction of a hydrogen from a neighbouring iPP chain. The remaining double bond on the DVB moiety of the latter can further take part in a similar formation of LCB-iPP (8).

The mechanism has been sketched simplified in this scheme. Other possible side reactions include: (i) direct coupling between two macro-radicals (3), (ii) H-abstraction with the initiator, (iii) reaction of the grafted product (7) with the macro-radical (3), (iv) transfer reactions of the radical species to the initiator or the monomer, (v) addition (followed by homopolymerisation) of the primary radical (2) with the monomer (DVB). Of all possible reactions the successive coupling of two macro-radicals (in the presence or not of the co-agent) is the most disadvantageous. If one considers the lower relative stability of the secondary and primary macro-radicals (and thus the probability of finding them instead of the tertiary), the chance for this coupling to give back a linear chain is very small. Coupling of tertiary free radicals, then, leads



Scheme 1. Schematic presentation of the reaction mechanism involving DVB. The other co-agents are expected to become involved in similar reactions.

to cross-linking of the iPP, the most undesired side-product.  $\beta$ -Scission must take place in the system, as demonstrated by blank experiments, to ensure that enough shorter iPP chains are created in situ. Whether these shorter chains (5) react directly with (7) or are formed after the coupling can not be easily established [16,17]. Shorter paraffinic chains with greater mobility, especially when they have a reactive end-group, show much higher reactivity than longer chains [18]. Therefore, high participation of short chains with double bonds

or free radicals at the end should be expected in the branching reactions.

### 3. Measuring the level of LCB

One of the difficulties in the studies on the addition of branches on linear polymers is that of the characterisation of the resulting structure. This characterisation is essential in evaluating the processing behaviour of the polymers. The molecular parameters that are important for the processing

properties include the average number of branches per molecule ( $B_n$ ), their topology (the distribution along the chain and their comb- or Cayley tree-type structure) and their lengths [19,7]. There are three main methods to characterise polymers for LCB: using triple-sensor GPC, using NMR and using rheology.

GPC is used for the fractionation of the polymer and the measurement of the hydrodynamic volume of the fractions, from which one can calculate the molecular mass and its distribution (MWD). Because a branched chain is more compact in a solvent than a linear chain with the same molecular mass, the intrinsic viscosity of a branched polymer is lower than the one of the equivalent linear polymer. Therefore, if the intrinsic viscosity of the fractions is measured as they come out of the column, then LCB can also be inferred by GPC [1]. For this reason different sensors (usually three) are used simultaneously at the eluent to determine independently the molecular weight and the intrinsic viscosity of the fractions. An estimate of the LCB level can be made then by using the theory of Zimm and Stockmayer [20].

The presence of branches can be detected by identification and quantification of NMR signals related to the branched structure. In the case of iPP, the measurement uses the resonance peaks of methine carbon atoms that correspond to branches longer than four or five C [21]. The drawback of this method is that it is difficult to distinguish directly the short from the long branches, if they coexist in the same sample. Further, the amount of LCB that is needed for the enhancement of the melt strength is far too small (in the order of one branch per  $10^5$  C atoms) to be detected in ordinary NMR measurements.

Rheology has proved to be a reliable method for the verification of the existence of long branches on the polymeric chain [19,22] and it is the easiest to implement. LCB increases the possibility for entanglements in the polymeric melt, and, thus, its elasticity. A similar effect, however, could result also from a broadening of the molecular mass distribution (MWD). Gathering information from a number of different techniques is necessary for unambiguous answers as to the molecular origin of the rheological changes.

Tsenoglou and Gotsis [23] have shown that the introduction of sparse LCB on linear PP chains at (almost) constant mass average molecular weight,  $M_w$ , increases the zero shear viscosity,  $\eta_0$ , of the

melt, something that is not true for broadening the MWD. The increase of  $\eta_{0,LCB}$  is related quantitatively to  $B_n$

$$B_n \approx \frac{\ln \left\{ \frac{\eta_{0,LCB}}{\eta_{0,L}} \right\}}{\alpha \left( \frac{M_w}{M_c} - 1 \right) - 3 \ln \left\{ \frac{M_w}{M_c} \right\}}, \quad (1)$$

where  $M_c$  is the molecular weight at the onset of entanglements ( $=13640$  g/mol for PP, Langston et al. [7]) and  $\alpha$  is a constant [23]. The method works only for polymers where the branches are the same as the backbone (same chain flexibility), where there is no significant change of the molecular weight upon modification, and for  $B_n \ll 1$ . It should be noted here that, upon increasing  $B_n$  above 1,  $\eta_0$  may go through a maximum and may start decreasing again [24]. A well known example is LDPE, which usually has a lower zero shear viscosity than HDPE with equivalent  $M_w$ .

A more detailed method to estimate LCB by comparing the zero shear viscosity of the linear and the branched polymer has been proposed by Janzen and Colby [24]. This method works even when the molecular weight changes. An average molecular weight between branches,  $M_b$ , was introduced to characterise LCB and the zero shear viscosity was related to  $M_w$  and  $M_b$

$$\eta_0 = AM_w \left[ 1 + \left( \frac{M_b}{M_c} \right)^{2.4} \right] \left( \frac{M_w}{M_b} \right)^s, \quad (2)$$

where  $A$  is a parameter that can be evaluated if  $\eta_0$  and  $M_w$  of the linear polymer are known. The exponent  $s$  is given for sparsely branched polymers by

$$s = \max \left[ 1, 1.5 + 1.125B \ln \left( \frac{M_b}{90M_{Kuhn}} \right) \right]. \quad (3)$$

$B$  is a constant. The Kuhn length,  $M_{Kuhn}$  for polypropylene is 187.8 g/mol [7].

For a branched polymer,  $M_b < M_w$ . The ratio  $M_b/M_w$  should decrease as the degree of branching increases, because more of the molecular weight corresponds then to the parts of chain between the branch points or to the branches themselves. The method has been tested with LDPEs and branched polyesters [24] and polypropylenes [7].

When compared to that of the equivalent linear chain polymer, the shape of the dynamic viscosity curve,  $\eta^*(\omega)$ , can also give information on the presence of LCB and the polydispersity. Increasing the polydispersity index,  $M_w/M_n$  the transition region

from the zero shear rate plateau to the power-law behaviour becomes broader. LCB has a similar effect. However, two points of inflection may appear within the transition zone in the latter case [25]. Thus, plotting the first derivative of  $\eta^*(\omega)$  vs.  $\omega$  will give us two peaks at these points, the relative heights (depths) of which could serve as semi-quantitative indices for LCB. Obviously, in order to use this method to characterise LCB accurately, high quality, noiseless data are needed for  $\eta^*(\omega)$ .

The activation energy for flow has been related (it decreases) with the degree of LCB ( $B_n$ ) by Vega et al. [26]. This relation, however, is not very sensitive to small values of  $B_n$  [1] and the method is not quantitative in this case.

The melt elasticity enhancement, as measured in small strain amplitude oscillatory shear flow, has been used by Wood-Adams and Dealy [22,25] to quantify LCB in metallocene catalysed polyethylenes with structures similar to the lightly branched polypropylenes of the present work. Two methods were tried, both with considerable success. In the first method [22], the apparent molecular weight distribution was estimated from the curves of the dynamic moduli using a modified version of the technique of Shaw and Tuminello [27]. This distribution was compared to the true MWD measured by GPC. The difference in the position of the maxima of the two MWD curves gave a quantitative indication of  $B_n$ .

In the second method, Wood-Adams and Dealy [25] examined the dynamic moduli ( $G'$  and  $G''$ ) of melts of linear and branched PPs. The presence of LCB adds a relaxation mode at low frequency, which is not present in the linear material. The changes of the storage modulus at low frequency can be used, therefore, as an indication of LCB in polybutadienes [28] and PP [29]. A more sensitive indicator of the changes in elasticity and the additional relaxation modes that LCB may induce is the loss angle ( $\tan \delta = G''/G'$ ). The curve of  $\delta(\omega)$  of a linear polymer in a semi-log plot has a convex curvature: The loss angle remains at values close to  $90^\circ$  at low frequencies, and starts decreasing monotonically at higher frequencies. The presence of LCB introduces two extra inflection points in the curve and the middle part of the curve becomes concave, sometimes leading, to an intermediate plateau. The gradual change of convex to concave and the relative height of this plateau can be related qualitatively to the increase of LCB on the polymer chains [25].

The best quantitative way to estimate the improvement of processing properties due to the addition of LCB on the linear chain is by directly measuring the strain hardening of the viscosity of the melt in uniaxial elongational flow,  $\eta_E^+(\epsilon; \dot{\epsilon})$  [30,31]. Indeed, in a series of peroxide-modified polypropylenes with increasing degree of long chain branches, Gotsis et al. [30] showed that both the onset and the extent of strain hardening increased with  $B_n$ . The whole  $\eta_E^+(\epsilon)$  curves could be described well by classical viscoelastic models that implemented a damping function with a parameter,  $\beta$ , which reflected the level of LCB in the fluid. Inversely, the value of  $\beta$  could be used to infer the value of  $B_n$  from the measured  $\eta_E^+(\epsilon)$  curve. However, accurate measurements in uniaxial elongational flows require samples of a few grams of material, which is more than what we produced in the present series of exploratory experiments.

The present report only screens some procedures and co-agents used to graft branches on PP by reactions in the solid state based on GPC and dynamic rheology results. Larger quantities of modified iPP can be produced using the chosen method when the screening has been completed. Measurements in uniaxial elongational flow can be conducted then to establish the actual improvement of the processing properties of iPP, those that are required in order to use this material efficiently in thermoforming, foaming or blow moulding applications.

## 4. Experimental part

### 4.1. Materials

The isotactic polypropylene was supplied by DSM, Geleen, in powder form (particle diameter of around 0.3 mm) with number average molecular weight ( $M_n$ ) of 70,000 g/mol, weight average molecular weight ( $M_w$ ) of 300,000 g/mol and polydispersity ( $M_w/M_n$ ) of 4.3. It was stored at  $0^\circ\text{C}$  since it did not contain any stabiliser. Divinylbenzene (DVB, Aldrich), 1,4-benzodiol (RES, Aldrich), furfuryl sulphide (FS, Aldrich) and *tert*-butyl perbenzoate peroxide (TBPB, Merck-Schuchard) were purchased as high-purity products (98%) and were used as received.

### 4.2. Branching reactions

The reagents, peroxide TBPB (37 mmol/kg polymer) and 0.1–0.3 wt% (with respect to PP) co-agent



(FS, DVB or RES), were dissolved in acetone and the mixture was added to 20 g sample of polypropylene powder. Acetone was chosen because it could dissolve the reagents but not the polymer. The removal of the solvent after the reaction was, thus, facilitated but the reactions took place only on the surface of the particles of the polymer. The polymer–solution mixture was kept in dark for approximately 12 h. Then the solvent was evaporated in a rotary evaporator. Impregnated PP deprived of solvent was put into glass ampules (about 5 g PP mixture/ampule) which were sealed in nitrogen atmosphere and let to react in an oil bath at 130 °C for 3.5 h (six half times of peroxide decomposition).

#### 4.3. Molecular weight and gel content determination

GPC (gel permeation chromatography) was used to determine the molecular weight (averages and distribution) of the polymers. The samples were dissolved in trichlorobenzene and filtered to remove the insoluble fraction, when present. The solution was then passed through a PL Gel 5 mL Mixed-A column of the chromatograph at 140 °C.

The non-decomposed peroxide and the low-molecular weight products of the decomposition of the peroxide and the co-agents were extracted from the modified iPP samples using water and ethanol and the samples were dried under vacuum to constant weight. Samples of  $m_1 \approx 1$  g were put into glass fabric bags and extracted in 100 cm<sup>3</sup> boiling xylene containing 0.05% hydroquinone. After extraction for 6 h the xylene solution was substituted by pure xylene and the extraction continued for another 6 h. Then the iPP samples were extracted with benzene for another 2 h. The extracted fabric bags were then vacuum dried to a constant weight, which corresponded to the insoluble (cross-linked) portion of the iPP sample ( $m_2$ ).

The proportion of cross-linked iPP was then determined from the relation:

$$\text{iPP cross-linked (in wt\%)} = \frac{m_2}{m_1} \times 100 = x\% \text{ iPP gel.}$$

#### 4.4. Rheological characterisation

Rheology was used for the qualitative estimation of the presence of LCB. The rheological measurements were conducted in a Rheometrics RMS 800 strain controlled rheometer, using plate–plate fix-

tures. The disk-shaped samples were prepared by compacting the sample powder in a hot press at 190 °C for about 15 min. The disks had a thickness of 1.0–1.5 mm and a diameter of either 8 or 25 mm. The samples were measured in small strain amplitude oscillatory shear flow at temperatures from 170 to 230 °C under nitrogen. The dynamic moduli,  $G'$  and  $G''$ , and the complex viscosity,  $\eta^*$  were measured as functions of the frequency. Each measurement lasted around 10 min. As seen from “time sweep” measurements in the same instrument, this time did not result in remarkable changes in the properties of the samples. Changes might have been caused by degradation or reactions due to the modifiers left in the polymer after the LCB grafting reactions of Section 4.2.

The dynamic rheological data were shifted horizontally along the frequency axis to the temperature of 200 °C, whenever this was possible. The time–temperature superposition was not successful for all samples, however. The failure of the superposition is typical for thermorheologically complex fluids, such as the long chain branched polypropylenes [7].

### 5. Results and discussion

Table 1 shows the solubility parameters of the different co-agents and that of iPP. It can be seen there that the compatibility of iPP with the co-agents is ranked as follows:

Compatibility: DVB > FS > RES.

Table 2  
List of synthesised samples

#	Peroxide (mmol/kg)	Co-agent type	Co-agent (wt%)	Gel (wt%)	$M_n$ (g/mol)	$M_w/M_n$
0	0	None <sup>a</sup>	0	0	72,500	4.2
0 <sup>b</sup>	0	None <sup>b</sup>	0	0	49,750	3.7
1	37	DVB	0.1	0.43	46,950	5.8
2	37	DVB	0.2	11.9	38,200	6.8
4	37	DVB	0.25	16.4	26,700	7.9
5	37	RES	0.1	0.36	55,600	5.5
8	37	RES	0.2	0.13	57,500	6.3
12	37	FS	0.1	0.22	50,400	7.2
13	37	FS	0.15	1.3	48,700	9.5
14	37	FS	0.2	0.17	47,050	9.5
100	37	RES <sup>c</sup>	0.25	n.m.	45,900	10.4

<sup>a</sup> Pure PP as received.

<sup>b</sup> PP subjected to the same thermal treatment as for the branched samples.

<sup>c</sup> Containing also 5 wt% styrene (with respect to the co-agent amount).

The synthesised samples are reported in Table 2 together with the GPC results and the gel content. This table indicates that even the simple thermal treatment of iPP at 130 °C for 3.5 h leads to a decrease of the molecular weight of the polymer. This is not surprising if one takes into account the  $\beta$ -degradation reaction of iPP at this temperature. Degradation leads to formation of smaller chains, which can further react through the action of a co-agent to form LCB-PP.

For our purposes and on the basis of the reaction mechanisms described in the previous section, it is sufficient to observe that an increase in the molecular weight averages ( $M_n$  and  $M_w$ ) relative to the blank experiment, together with a low gel content, represents an indication of LCB formation and not cross-linking. In this respect, Table 1 shows that the use of DVB as co-agent resulted mainly in cross-linking of iPP, as seen from the significant amounts of gel. On the other hand, the use of RES and FS clearly resulted in an increase of the molecular weight without formation of any significant amount of gel, thus, strongly suggesting the formation of LCB.

These preliminary conclusions have been confirmed by the rheological analysis, which was used as a tool to gain more detailed information on the molecular structure of the modified polymers. Figs. 1, 2, 4 and 5 display the curves of the dynamic moduli

( $G'$  and  $G''$ ) as functions of the measurement frequency for the original iPP and several modified samples.

The original iPP shows the typical curves for the moduli of a viscoelastic melt with low elasticity (Fig. 1). At low frequencies  $G'$  is lower than  $G''$ . The inverse of the frequency where  $G'$  crosses over  $G''$  is a characteristic relaxation time for the polymer. In the present case  $t_{cr} = 0.02$  s.

When DVB is used as co-agent the shape of the  $G'(\omega)$  curves remains the same but the moduli are considerably lower than those of iPP over the whole frequency range (Fig. 2). The viscosity decreases, without any enhancement of the elasticity, suggesting that the use of DVB results in overall degradation of the sample. The increase of  $\eta^*(\omega \rightarrow 0)$  could be an indication of some branching but, in combination with the measured gel content of these samples it also hints at increasing cross-linking of the polymer. All this is consistent with the gel content data (Table 2) and the GPC data (Fig. 3), which show that the molecular weight decreases almost linearly with the amount of DVB used for the modification.

At low levels of DVB, the destructive effect of the peroxide prevails. At higher levels the amount of cross-linked iPP increases, incorporating in the network mostly longer chains [10]. This is responsible for the decrease of the mean molecular weight of

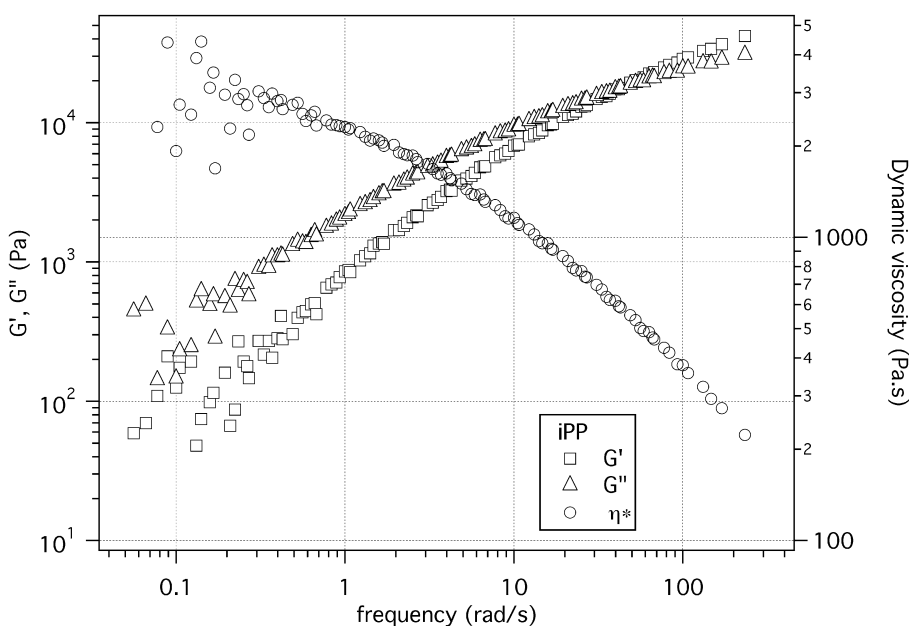


Fig. 1. Dynamic moduli of the original (linear) iPP (shifted at 200 °C).



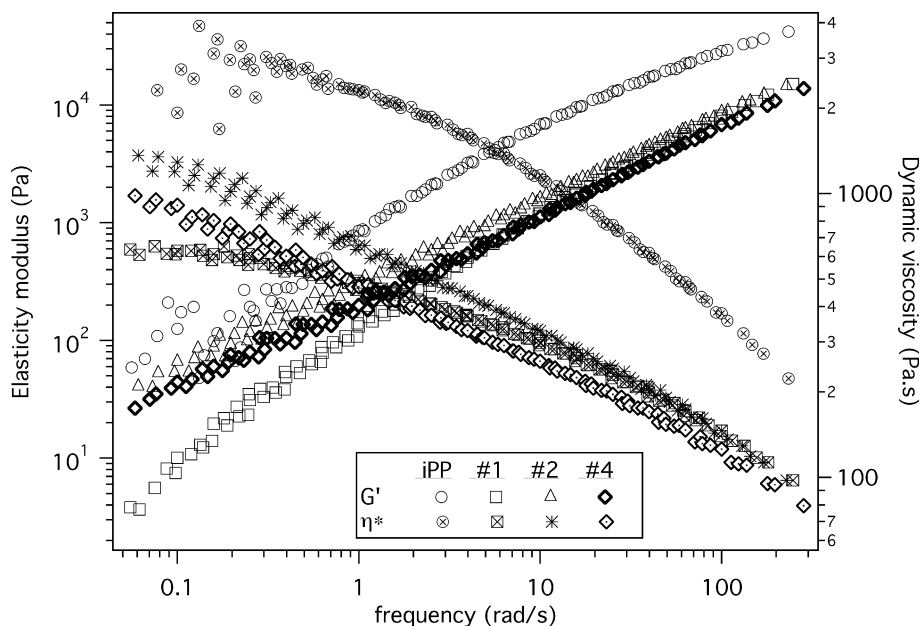


Fig. 2. Elasticity modulus,  $G'(\omega)$ , and viscosity,  $\eta^*(\omega)$ , curves for iPP modified with the DVB co-agent (shifted at 200 °C).

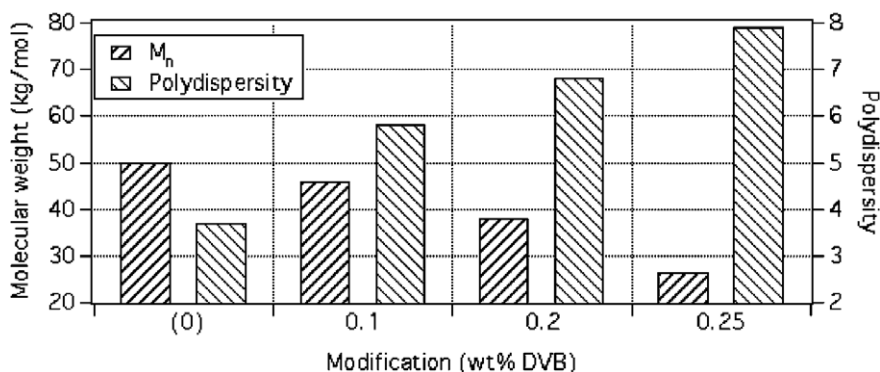


Fig. 3. Molecular weight of the modified samples as function of the DVB amount.

the non-cross-linked (soluble) part of the modified PP in this case. The existence of the network (gel) is the reason for the lower slopes of the  $G'(\omega)$  curves at low  $\omega$  in Fig. 2.

Extensive degradation of iPP was not observed when RES was used. The  $G'(\omega)$  and  $\eta^*(\omega)$  curves of the modified samples (Fig. 4) closely resemble the one for the original PP, not only in shape but also in absolute values. At higher amounts of RES there is a small reduction of the slope of  $G'(\omega)$  at low  $\omega$  and the increase and shifting of the Newtonian plateau in  $\eta^*(\omega)$  to lower  $\omega$ , hinting to the possible creation of some long branches or the beginning of cross-linking.

All samples modified in the presence of FS show higher values for  $G'$  with respect to the original iPP (Fig. 5). The same is true also for the sample modified with RES in the presence of styrene monomer. The slope at low frequencies is lower for all these curves and decreases when the amount of FS used increases. The zero frequency dynamic viscosity increases with the amount of co-agent used. The form of the curve changes and the shadow of two inflection points (around 15 and 0.5 rad/s) starts appearing in the logarithmic plots. On the other hand the molecular weight of these samples is not significantly higher than the one of the linear iPP. These are indications that, when FS is used as a

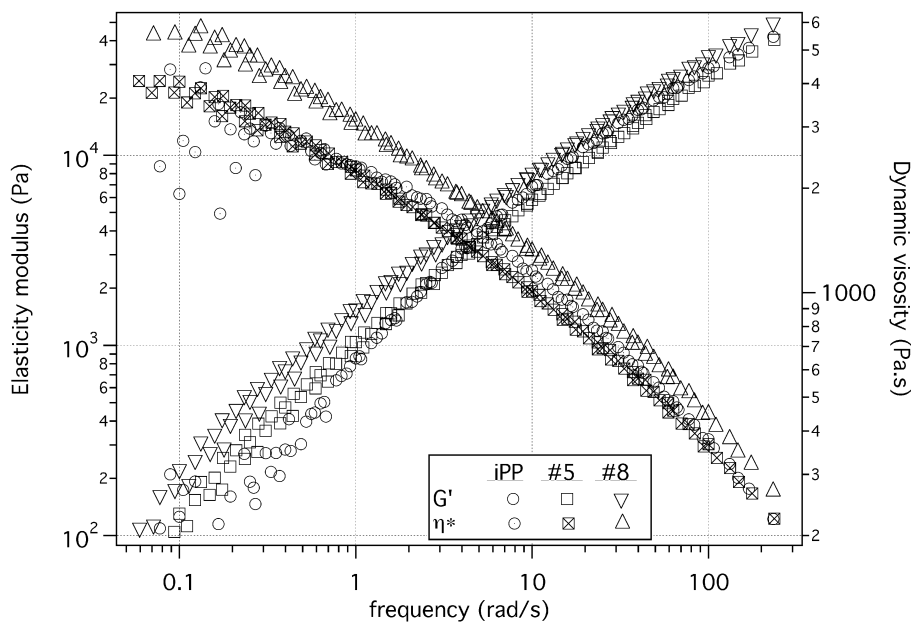


Fig. 4. Elasticity modulus,  $G'(\omega)$ , and viscosity,  $\eta^*(\omega)$ , curves for iPP modified with RES co-agent (shifted at 200 °C).

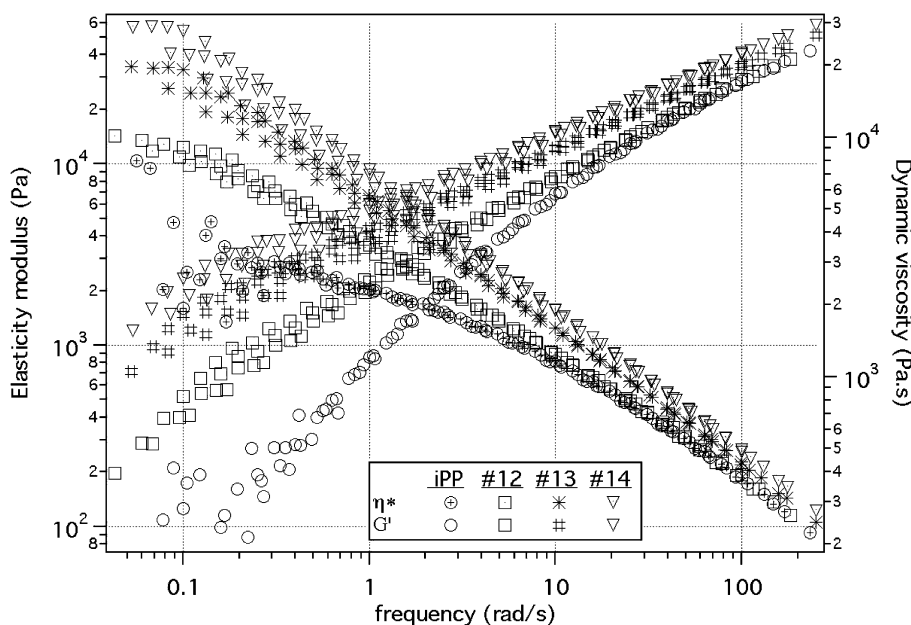


Fig. 5. Elasticity modulus,  $G'(\omega)$ , and viscosity,  $\eta^*(\omega)$ , curves for iPP modified with FS co-agent (shifted at 200 °C).

co-agent in the modification reaction, it induces long chain branching with no significant cross-linking.

In summary, as  $\omega \rightarrow 0$ , the  $G'(\omega)$  curves of the samples containing DVB (0.2 and 0.25 wt%), FS (all) and the one with RES (0.25 wt%) and styrene

(5 wt%) have a logarithmic slope lower than the one of the linear polymer. In non-filled systems this can be attributed either to cross-linking or to branching. On the basis of the GPC data one can rule out the possibility of branching when DVB is used. At the same time, this is a strong indication

that LCB are formed when FS is used as a co-agent or when RES is used in combination with styrene. In the following we will try to quantify the amount of LCB that is obtained by each co-agent.

### 5.1. Ranking the ability of the co-agents to induce LCB

In order to use the methods that compare the zero shear rate viscosities, the value of  $\eta_0$  can be estimated by extrapolation to zero rate using, e.g., the Cross viscosity model

$$\eta(\dot{\gamma}) = \frac{\eta_0}{1 + (\lambda\dot{\gamma})^n}. \quad (4)$$

Since the generation of branched structure during reaction at the solid state also results in different molecular weights of the samples, the application of the method proposed by Tsenoglou and Gotsis [23] is not straightforward. One way to circumvent the differences in molecular weight is to normalise  $\eta_0$  by  $M_w^{3.4}$  for the comparison, assuming that

$$B_n \propto \frac{\eta_0}{M_w^{3.4}}.$$

The values of this parameter for the samples are shown in Table 3.

With the assumption that the relative values of  $\eta_0/M_w^{3.4}$  for the reacted samples can be associated with  $B_n$ , at least when the same linear original polymer and similar modification reactions are used, the second column of Table 3 could indicate that the

samples modified in the presence of 0.25 DVB, 0.1, 0.15, 0.2 FS, or 0.25 RES with 5% styrene have some long branches. FS seems to be the most efficient, with the more used, the higher the resulting LCB. However, this can be used only as an indication. In reality,  $B_n$  depends but is not proportional to this ratio Eq. (1), and the validity of all the assumptions mentioned in Section 3 cannot be verified in the present case.

Similar conclusions can be drawn when applying the method proposed by Janzen and Colby [24] to the present data. The values of the constants in Eqs. (2) and (3) were evaluated either from the linear iPP data ( $A = 0.57 \times 10^{-5}$ ) or taken from [7] ( $B = 6$ ). The results are shown in the third column in Table 3 in the form of  $M_b/M_w$ . Values of this ratio above 1 are not accepted. The first three samples in the table lie outside the range of applicability of the method. The samples from the fourth row downwards all show  $M_b/M_w < 1$  and are decreasing in the same order as above.

Values of  $M_b$  close to  $M_w$ , as shown in Table 3 indicate sparse branching. A decreasing value of the ratio indicates increasing values of  $B_n$ . The trends seen from the comparison of the shear viscosity using either of these methods, however, cannot be considered as definite and have to be verified with other methods.

Branched polymers show higher melt elasticity as compared to their linear equivalents because the probability for entanglements increases with LCB. Enhancement of the elasticity can also be due to the presence of a broader molecular weight distribution. A quantitative idea of the melt elasticity for the present samples can be obtained from the crossover frequency ( $\omega_{cr}$ ), where  $G'$  becomes higher than  $G''$  (e.g., at around 50 rad/s for the linear iPP in Fig. 1). For some samples, this is reported in Table 3.

The inverse of  $\omega_{cr}$  is equivalent to a characteristic relaxation time of the material. Longer times (lower  $\omega_{cr}$ ) indicate higher elasticity and, indirectly, branching. It is clear from the table that samples prepared in the presence of FS (at all contents) and with RES in combination with styrene are more elastic than the original iPP. Although this could possibly be due also to the broader molecular weight distribution (both effects could result from the reactions proposed in Scheme 1 and might play a role here), it is in agreement with the results of the elasticity moduli and the viscosity. A confirmation of this comes from the fact that the use of DVB results in a decrease of the relaxation time  $1/\omega_{cr}$  in

Table 3  
Elasticity parameters of synthesised samples

PP (w/mmol/ kgPP)	$\eta_0/M_w^{3.4} \times 10^{-13}$	$M_b/M_w$	$\omega_{cr}$ (rad/s)	Notes
Pure <sup>a</sup>	0.7	Linear	50	–
DVB 0.1	0.2	1.06	>300	–
DVB 0.2	0.6	1.01	>300	–
DVB 0.25	0.9	0.98	n.d.	$G' < G''$ at all $\omega$
RES 0.1	0.9	0.97	80	–
RES 0.2	1.1	0.99	50	–
RES 0.25 <sup>b</sup>	–	–	n.d.	$G' > G''$ at all $\omega$ no $\eta_0$ could be defined
FS 0.1	1.5	0.97	20	
FS 0.15	2.2	0.94	8 and 0.08	Two crossovers, $G' > G''$ at low and high $\omega$
FS 0.2	4.5	0.93	(0.05)	$G' > G''$ at all $\omega$

<sup>a</sup> Pure PP as received.

<sup>b</sup> Containing also 5 wt% styrene (with respect to the co-agent amount).

**Table 3.** This is due to the reduction of the chain length which, in turn, decreases the possibility for entanglements.

Another way to investigate the presence of LCB involves the examination of the loss angle  $\delta = \arctan(G''/G')$ . Obviously, the lower the value of this angle, the more solid-like (i.e., elastic) the material at the corresponding frequency. The plot of the loss angle vs. the frequency is reported for all the samples in Fig. 6.

The original iPP displays indeed a monotonically decreasing curve of  $\delta(\omega)$ . The limit of  $\delta(\omega \rightarrow 0)$  is  $90^\circ$ , as the melt is a viscous liquid at infinite times. The value of the loss angle goes to zero at infinite frequencies, where the material responds as an elastic solid. As soon as some modification takes place the curve changes in position and in form.

The curves of all the samples that have been modified in the presence of FS (#12, 13, 14, 17) show much lower values for  $\delta$  than the curve for iPP, indicating higher elasticity at the same frequencies. As the amount of FS increases, the curve starts to show a deflection and then a local plateau at around 10 rad/s. If the system is not cross-linked the loss angle must eventually go to  $90^\circ$  as  $\omega \rightarrow 0$  but our measurements do not go to very low frequencies.

This behaviour in combination with the absence of any significant gel amounts leads to the conclusion that iPP samples modified using FS as co-agent have a lightly branched structure. The degree of branching seems to increase with the amount of FS present. The only sample that deviates from this trend is the one that used 0.3% FS. It seems that there is a optimum in the amount of co-agent for branching and any amount above this has an adverse effect on the probability of branch addition.

The examination of the RES co-agent is not as clear as the previous one. It is questionable whether the sample with 0.1 wt% RES displays an inflection (Fig. 6). Only in the curve of the sample modified with 0.2 wt% RES (#08) is there a hint to the presence of an inflection, and this sample may contain some very few branches. Sample #100, which was modified in the presence of 0.25% RES and 5% styrene shows very low values of  $\delta$  and a local maximum. This, in combination with the absence of a measurable amount of gel indicates that it has a branched structure.

The  $\delta(\omega)$  curves of the samples modified using DVB as co-agent (#01, 02, 04) lie mostly above the one of the original iPP. The elasticity of these samples, therefore, has been reduced by the modification.

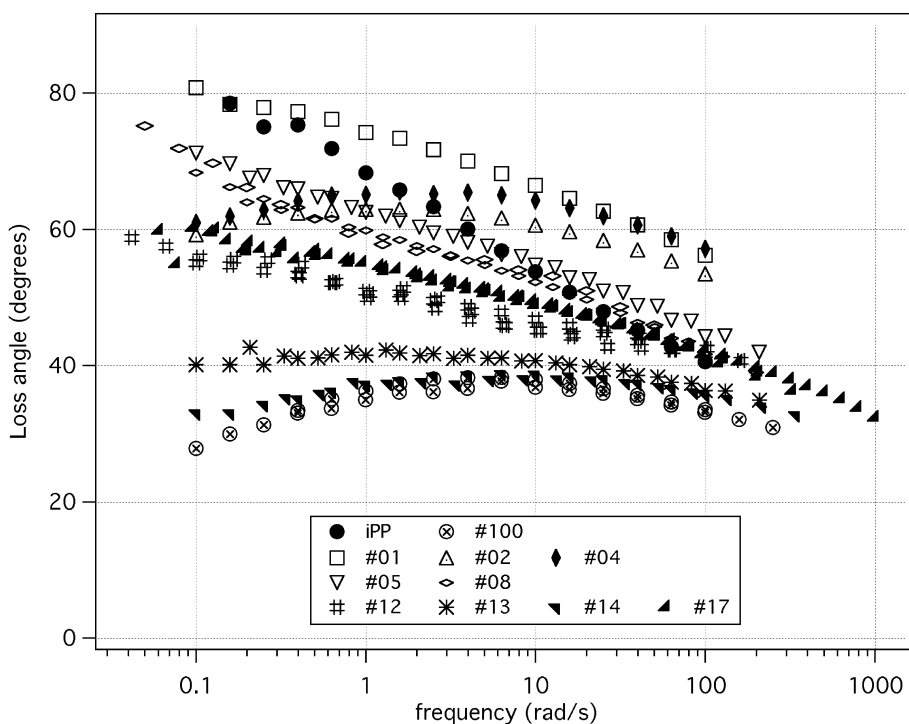


Fig. 6. Loss angle,  $\delta$ , as a function of frequency. The coding of the samples is the same as in Table 2.

The local maxima shown by #02 and #04 are due to the presence of high levels of gel (Table 2). There is no clear indication, therefore, whether this co-agent can induce a true branched structure to the bulk of iPP.

Summarising the above, it seems that DVB induces mostly cross-linking of iPP, which prevails over LCB; RES induces long chain branching when used above 0.2 wt% or in combination with styrene; and FS induces the formation of LCB at all concentrations used. It should be more correct, however, to compare the different co-agents on the basis of the same molar fraction instead of wt%. Taking the different molecular weight of the co-agents into account one can establish the following ranking of the co-agents regarding their ability to induce LCB  $FS > RES(+styrene) > RES \gg DVB$ .

The different efficiencies of the co-agents in grafting iPP and in inducing the subsequent long chain branching, as documented in the present results, can be understood from their different expected reactivities and different solubility in iPP. DVB is a self-polymerisable monomer, it is quite soluble in iPP and its double bonds can react very easily with the free macro-radicals that are formed on the iPP chains, resulting in grafted iPP. However, in our iPP reaction systems we usually obtain iPP grafted with DVB chains. Each DVB chain, even though it is short, represents a high local concentration of double bonds. This causes the formation of knots of cross-linking iPP. The present results have shown that insoluble cross-linked gel was produced also at very low content of DVB.

The polar co-agents FS and RES, which are not considered as polymerisable monomers (they are more reactive towards iPP than towards themselves), proved to be more effective co-agents for branching iPP. These co-agents are less reactive and less soluble in iPP than DVB. However, they fulfil the basic conditions for a co-agent: they can be grafted on the iPP chains and, therefore, enable the branching reactions. This was documented also by the increase of the molecular weight of the original iPP samples in these cases.

During the branching reactions many macro-radicals can be formed simultaneously along the same iPP chain. Besides grafting, the iPP chains undergo also  $\beta$ -scission (Scheme 1), something which is compatible with the observed lowering of the  $M_n$  and the broadening of the molecular weight distribution (Table 2). In the case of RES used together with sty-

rene as a second co-agent (as a reactive solvent for increasing the solubility of RES) the highest value for the polydispersity index  $M_w/M_n$  was 10.4. The beneficial influence of styrene on the branching of iPP using RES as co-agent is probably due to the “quenching” of highly reactive macro-radicals by styrene molecules. The resulting free radicals stabilised with benzylic-resonance have longer life time and, thus, a greater chance to meet a iPP fragment originating from the  $\beta$ -scission of iPP chains and form a branch, than the original macro-radicals.

## 6. Conclusions

The present work showed that it is possible to produce LCB-iPP via solid state modification. This represents, to our knowledge, a first attempt in this direction, i.e., to combine the positive properties of the solid state chemical modification with the production of a LCB-iPP. Analysis of the samples by GPC, determination of the gel content and rheological characterisation allow the ranking of the significance of the three possible processes (i.e., degradation, cross-linking and branching) with respect to the kind of co-agent used.

- The use of DVB results mostly in cross-linking of the iPP. As a very reactive polyfunctional monomer, DVB provides knots for the formation of an iPP network. During the polymerisation of DVB in iPP the functionality of the knots increases. Even at very low contents of DVB the formation of cross-linked PP cannot be prevented.
- The RES is effective only at high concentration (0.2 wt%) or in combination with styrene as comonomer.
- The presence of FS induces LCB at all investigated concentrations (0.1–0.2 wt%).
- A preliminary ranking for the efficiency of the co-agents is

$FS > RES(+styrene) > RES \gg DVB$ .

- The differences in the efficiency of the co-agent to induce LCB can be explained on the basis of the difference in the values of the solubility parameter of the co-agents and iPP. Some solubility of the co-agent in iPP is necessary. The success of the branching of PP, however, depends also on the possibility to suppress the cross-linking reaction. Polymerisable multifunctional monomers are not suitable to induce LCB.

- An intermediate value of the solubility parameter (i.e., not too close to the one of iPP but also not too different) represents a first criterion for the choice of the co-agent.

A more accurate understanding of the chemical mechanism involved in the process could be gained by taking into account also the different reactivity of the co-agents. Such study, as well as, a parallel one involving the use of other co-agents and peroxides is currently under way in our three institutes.

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